

Original Research Article

## INFRA-RED ABSORPTION INTENSITIES

Dr. Achal Kiran<sup>1\*</sup>, Kajal Chavda<sup>2</sup>

Department of Physics, Surendranagar University, Gujarat

<sup>1</sup> \*Assistant Professor, Surendranagar University (Gujarat).

<sup>2</sup> Research Scholar, Surendranagar University (Gujarat).

**\*Corresponding Author:** - Dr. Achal Kiran

\*Assistant Professor, Department of Physics, Surendranagar University, Gujarat

### Abstract

This paper deals with the intensity measurements and absorption bands are characterised not only by their frequency but also by intensities and band shape. The attenuation of the intensity of a monochromatic beam of frequency  $\nu$  is proportional to intensity then we can write,  $I^\nu = I_0^\nu \exp(-\epsilon^\nu cl)$ .

Absorption bands are characterised not only by their frequencies but also by band shapes and intensities. More will be said about band shapes in Next Chapter. Intensity measurements have considerable intrinsic use and importance, but due to experimental difficulties in measuring true, or absolute, intensities their use has been very restricted in the past.

First of all we must define what is meant quantitatively by intensity. If we accept reasonably postulates that the attenuation of the intensity of a monochromatic beam of frequency  $\nu$  is proportional to the light flux, or intensity, of radiation of that frequency and to the number of absorbing centres ( $c \cdot l$  where  $c$  is the concentration of absorbing material and  $l$  is the path length through the medium) then we may write  $dI^\nu = -\epsilon^\nu I^\nu c dl$ , or on integrating

$$I^\nu = I_0^\nu \exp(-\epsilon^\nu cl) \quad (8.1)$$

$I_0^\nu$  is the initial beam intensity and  $\epsilon^\nu$  is a parameter which is fixed for a given radiation frequency and a given absorbing medium (absorption coefficient). Solving for  $\epsilon^\nu$  we have

$$\epsilon^\nu = \frac{1}{cl} \log_e \left( \frac{I_0^\nu}{I^\nu} \right)$$

Of course any absorption band has a finite frequency spread, or band width. We can define a constant for a band

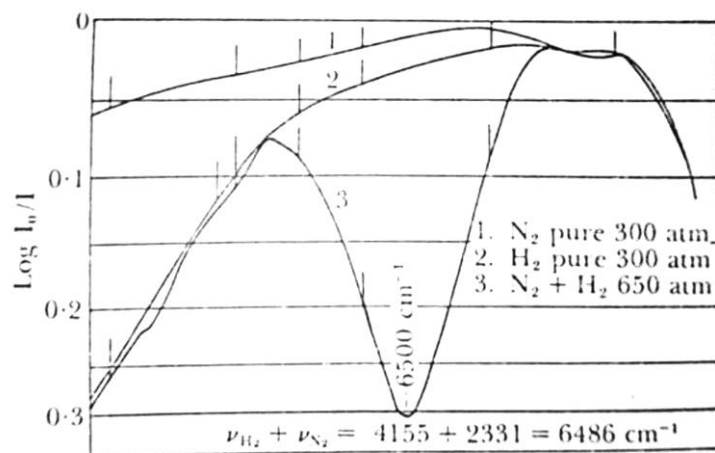
$$\int \epsilon^\nu d \log_e \nu = \frac{1}{cl} \int \log_e \left( \frac{I_0^\nu}{I^\nu} \right) d \log_e \nu = \Gamma$$

As the band intensity where the integration is taken to extend over the entire band. It used to be standard practice to define the intensity as the

Other indirect techniques of measuring infra-red absorption intensities exist. These are of generally limited applicability but have been of considerable importance in establishing reliable values for the intensities in the spectra of many simple compounds. One method suited for simple molecules with strong, well separated absorption bands is the study of the dispersion of infra-red rays. A vibrating electric moment in a molecule gives a contribution to the refractive index of

$$\Delta_i(n-1) = \frac{N}{6\pi^2c} \left( \frac{\delta\mu}{\delta Q_i} \right)^2 / \nu_i^2 - \nu^2 \quad (8.2)$$

Where  $n$  is the refractive index,  $\nu_i$  is the frequency of the vibration  $i$ ,  $\nu$  is the frequency of the incident light,  $N$  is Avogadro's number and  $\delta\mu/\delta Q_i$  is the transition dipole. (The above formula, as the Kramers-Heisenberg



**Fig.8.2** Simultaneous infra-red transition in mixtures of  $N_2$  with  $H_2$

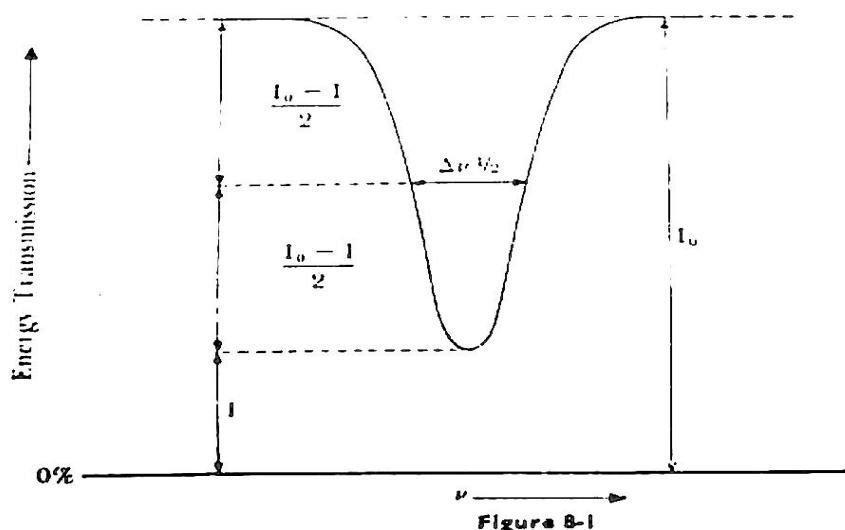
(as observed with an optical path length of about 10 metres).

Integral with respect to  $\nu$  but the former definition is more satisfactorily related to molecular parameters.

Clearly to measure intensities the following experimental conditions must be met with.

- The energy reaching the detector should be reasonably monochromatic. Obviously some spread in frequency is unavoidable as one can not reduce the frequency range indefinitely, even if the monochromator would allow, and still have sufficient energy to produce a sensible signal from the detector. The practical definition of reasonably monochromatic in this context is that the frequency spread should be small compared with the half band width of the band being measured. The half band width is the frequency difference the two points where the extinction coefficient,  $e$ , has a value half of its maximum (see figure 8-1).
- The recorded signal from the detector must be linearly proportional to the energy falling on the detector. Modern infra-red spectrometers are very satisfactory in this respect and this condition does not usually present difficulties.

In infra-red spectroscopy condition (a) is generally difficult to meet, particularly for the narrow bands of solids and gases. The effect of finite slit widths is to give a low value for the integrated intensity. For example the measured intensity of a square wave of width  $2 \text{ cm}^{-1}$  and with a true absorbance of 50 per cent will be 20 per cent low using a slit width of  $5 \text{ cm}^{-1}$ . For real band shapes and for higher intensities the discrepancies are greater.



### INFRA-RED ABSORPTION INTENSITIES:-

Formula, assumes that the absorption line is infinitely narrow, and has to be modified slightly for finite line widths.)

Now as we shall see the infra-red absorption intensity is related to the dipole derivative  $\frac{d\mu}{dQ_i}$ , by

$$\Gamma_i = \frac{N\pi}{v_t} \frac{N\pi}{3c} \left( \frac{\delta\mu}{\delta Q_i} \right)^2 \quad (8.3)$$

Thus the vibrational contribution to the refractive index is simply related to the infra-red absorption intensity, and in fact, both are manifestations of the same property. The particular advantage of the dispersion method, as can be seen from equation (6.2), is that even for infinitely narrow absorption lines the change of the refraction with frequency is gradual. A typical refraction spectrum due to two rotational vibrational bands of  $H^{35}Cl$  and  $H^{37}Cl$  is shown in figure 8-3.<sup>39</sup>

Details of a large sensitive refractometer constructed for such studies are to be found in *Advances in Spectroscopy*.<sup>40</sup> A monochromator produces a beam of monochromatic radiation which is passed through a hollow prism. The deviation of the beam, or more usually the change in the angle of minimum deviation on filling the prism with the compound to be investigated, permits the refractive index to be deduced. The refractometer previously referred to has an accuracy of about  $3 \cdot 10^{-3}$  seconds. As already mentioned the previous discussion has assumed the line to be infinitely narrow. For real absorption the effect of absorption and of finite band width must also be considered and the procedures and theory become more complicated. A more advanced text on dispersion theory is *Infrared Spectroscopy and Molecular structure*.<sup>41</sup>

A further method of measuring intensities is known as the curve-of-growth method. In this method measurements are made at different path lengths. By assuming a certain band shape the error due to finite slit widths can be eliminated. For instance let us assume that the individual bands have Lorentzian shapes. This means that the shape of a band is related to its half height width,  $\Delta v^{1/2}$ , by

$$\log \left( \frac{I_0}{I} \right)_v = K \frac{\Delta v_{\frac{1}{2}}}{(v - v_0)^2 + \left( \frac{1}{2} \Delta v_{\frac{1}{2}} \right)^2}$$

Where  $v_0$  is frequency at the band centre and  $I_v$  is the intensity of transmitted radiation at the frequency  $v$ . Such a band shape is predicted where radiation damping or collision broadening are the shape determining processes. The true integral over frequency of the fraction of energy absorbed from the beam is equal to the observed. This must be true for any slit and band shape as can be seen by examining the previous example.

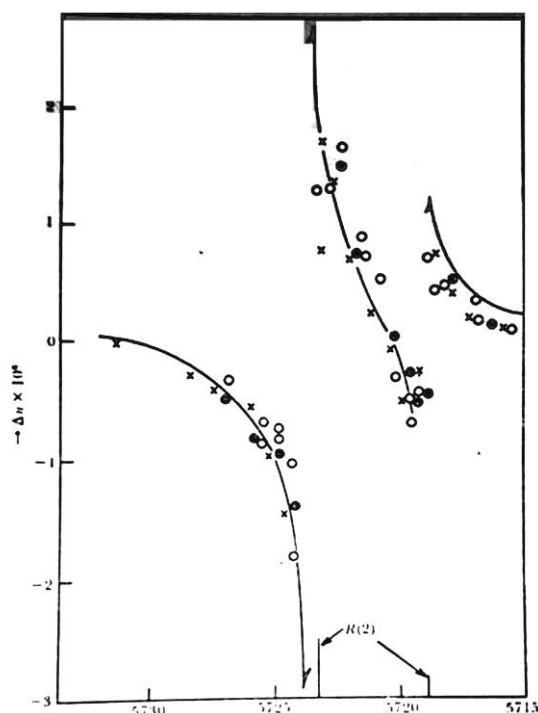
Let

$$\int \frac{T_0 - T}{T_0} dv = \int \frac{I_0 - I}{I_0} dv = W$$

Then for a Lorentzian band shape

$$W = 2\pi \frac{\Delta_{\frac{1}{2}} x e^{-x}}{2} [J_0(ix) - iJ_1(ix)] \quad (8.4)$$

An



**Fig. 8.3** The vibration-rotation contribution to the refractive index by the R(2) bands of the 2-0 vibrational transitions for  $H^{35}Cl$  and  $H^{37}Cl$ .

$$x = c\Gamma vl/2\pi \Delta v_{1/2} \quad (8.5)$$

Where,  $c$  is the concentration of absorbing material

$I$  is the true line intensity,  $\Delta v_{1/2}$  is the line half width,

$J_0$  and  $J_1$  are zero and first order Bessel functions, and  $l$  is the path length of absorbing material.

### INFRA-RED ABSORPTION INTENSITIES

By making measurements of  $W$  at two or more path lengths at a constant concentration then (8.4) and (8.5) can be solved for  $I$ . Unfortunately, for this method to be applicable it is necessary to resolve the individual rotational lines in the vibrational-rotational band. Where this can be done the method is of high accuracy. Furthermore, when the individual rotational lines can be resolved the Wilson-Wells procedure is generally less applicable.

These points are demonstrated by the history of the measurements of the intensity of band at  $670 \text{ cm}^{-1}$  in gaseous  $CO_2$ . Prior to 1956 the Wilson-Wells procedure gave values of 5.4 to 6.3 in units of  $10^3 \text{ cm}^2/\text{mole}$ . Kaplan and Eggers<sup>42</sup>, using the curve-of-growth method, arrived at a value of 8.07. However, they pointed out that this band is an extremely difficult band to study by the Wilson-Wells method since (a) it has a great deal of its intensity concentrated in a sharp  $Q$  branch with a half width of only  $0.35 \text{ cm}^{-1}$  and (b) to measure it, it is necessary to remove absorption due to atmospheric carbon dioxide. Subsequent work in which the Wilson-Wells procedure was used, with particular attention being paid to these points, led to a value of 8.09 units.<sup>43</sup> The pressure of broadening gas which had to be employed to give adequate pressure broadening was 68 atmospheres, but no evidence of induced absorption was found. This demonstrates the care which must be exercised in making intensity measurements.

As has already been emphasized the major difficulty in measuring the intensities of absorption bands of gaseous materials arises because of the sharp  $Q$  branches. Provided that the direction of the transition moment with respect to the molecular axes is known then the shape of the band in the absence of perturbations such as Fermi resonance can be computed. Comparison of the observed  $P$  and  $R$  band maxima with the calculated shape factor in these regions permits the derivation of the transition moment and hence the band intensity.<sup>44</sup>

**References:**

1. C. Secroun and P. Jouve, *J. Phys. (Paris)* 32, 871 (1971).
2. R. A. Toth, *J. Mol. Spectrosc.* 46, 470 (1973).
3. Y. Y. Kwan, *J. Mol. Spectrosc.* 49, 27 (1974).
4. D. Z. Robinson, *J. Chem. Phys.* 19, 881 (1951).
5. H. Yamada and W. B. Person, *J. Chem. Phys.* 45, 1861 (1966).
6. R. A. Toth, R. H. Hunt and E. K. Plyler, *J. Mol. Spectrosc.* 35, 110 (1970).
7. E. W. Kaiser, *J. Chem. Phys.* 53, 1686 (1970).
8. P. R. Bunker, *J. Mol. Spectrosc.* 45, 151 (1973).
9. R. A. Toth, R. H. Hunt and E. K. Plyler, *J. Mol. Spectrosc.* 38, 107 (1971).
10. D. F. Eggers and B. L. Crawford Jr, *J. Chem. Phys.* 19, 1554 (1951).
11. R. J. Corice, K. Fox and G. D. T. Tejwani, *J. Chem. Phys.* 59, 672 (1973).
12. (a) S. A. Francis, *J. Chem. Phys.* 18, 861 (1950); (b) H. Luther and E. Czerwony, *Z. Phys. Chem.* 6, 286 (1956).